Alkylation of Iridium via Tandem Carbon−Hydrogen Bond Activation/Decarbonylation of Aldehydes. Access to Complexes with Tertiary and Highly Hindered Metal−Carbon Bonds

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Reactions between Cp*(PMe_3)Ir(Me)OTf (**1**) and aldehydes (RCHO) proceed with high selectivity to give the hydrocarbyl carbonyl salts [Cp*(PMe_3)Ir(R)(CO)][OTf] (R = Me (**2**), Et (**3**), *n*-Pr (**4**), c-Pr (**5**), Ph (**6**), 1-ethylpropyl (**7**), *p*-tolyl (**8**), mesityl (**9**), 2-(*Z*)-1-phenylpropenyl (**10**), vinyl (**13**), *t*-Bu (**14**), 1-adamantyl (**17**)). This tandem C−H bond activation/decarbonylation reaction provides access to the first isolated tertiary alkyl complexes of iridium. X-ray diffraction studies were performed on mesityl complex **9**, *tert*-butyl derivative **15**, and 1-adamantyl compound **18**. Decarbonylation of cyclopropyl complex **5** results in irreversible opening of the cyclopropyl ring. This reaction has provided useful information concerning the mechanism of C−H activation of cyclopropane by **1**. Hydride reduction of the *p*-tolyl carbonyl salt **8** has provided an example of a rare transition-metal formyl complex, Cp*-(PMe_3)Ir(*p*-tolyl)(CHO) (**28**).

Introduction

Significant advances have been made since the initial discovery of transition-metal complexes that are capable of intermolecular cleavage of the carbon−hydrogen bonds in saturated hydrocarbons.[1−13] We recently discovered a stoichiometric system that thermally activates the C−H bonds of methane, as well as other hydrocarbons and simple organic molecules, at unprecedentedly low temperatures.[14,15] This system utilizes the iridium(III) complexes Cp*(PMe_3)Ir(Me)OTf (**1**) and [Cp*(PMe_3)Ir(Me)(CH_2Cl_2)][BAr_f] (BAr_f = B(3,5-$C_6H_3(CF_3)_2)_4^-$) as precursors of the highly reactive cationic species [Cp*(PMe_3)Ir(Me)]$^+$.[16] In addition to our initial studies aimed at exploring the scope and limitations of reactions of **1** (and its BAr_f salt) with organic substrates,[14,15,17] we have focused our efforts on the utilization of this interesting class of reactions for the synthesis of unusual organometallic complexes of structural and mechanistic consequence. For example, recent work in our group has shown that **1** can be used to access iridium Fischer carbene and carbyne complexes.[18,19] In the present report we describe the synthesis of tertiary alkyl and cyclopropyl substituted iridium complexes by a tandem C−H activation/carbonyl migratory deinsertion reaction of triflate complex **1** with aldehydes, as well as further derivatization reactions of the products of the tandem reaction.[20]

Results

Reaction of 1 with Aliphatic and Aromatic Aldehydes: Synthesis of Cationic Hydrocarbyl Carbonyl Complexes. Addition of 1 equiv of aldehyde (RCHO) to dichloromethane solutions of Cp*(PMe_3)Ir(Me)OTf (**1**) at room temperature results in rapid evolution of methane and the formation of the cationic hydrocarbyl carbonyl complexes [Cp*(PMe_3)Ir(R)(CO)][OTf] (R = Me (**2**), Et (**3**), *n*-Pr (**4**), c-Pr (**5**), Ph (**6**),

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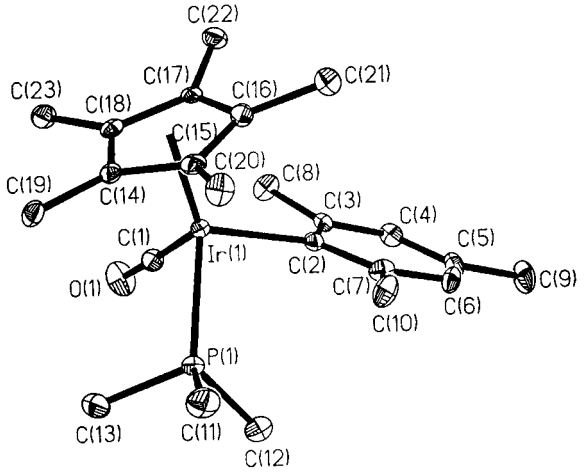
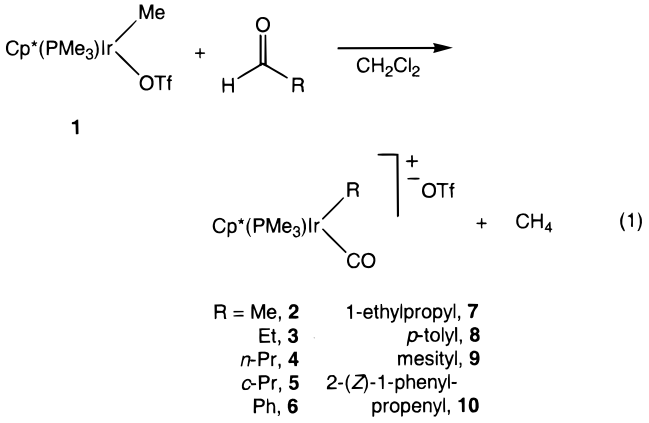


Figure 1. ORTEP plot of the solid-state molecular structure of the major component of the cationic portion of [Cp*-(PMe_3)Ir(mesityl)(CO)][OTf] (**9**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

1-ethylpropyl (**7**), *p*-tolyl (**8**), mesityl (**9**), 2-(*Z*)-1-phenylpropenyl (**10**)) (eq 1). Complexes **2**−**10** exhibit similar



^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectra as well as ν_{CO} infrared stretching frequencies. In the ^{1}H NMR spectra of **2**−**10** the resonances for the Cp* ligands appear at δ 1.94−2.08 ($^4J_{P-H}$ = 2.0−2.4 Hz) and the trimethylphosphine protons resonate at δ 1.69−1.86 ($^2J_{P-H}$ = 10.8−11.2 Hz). The ^{31}P{^{1}H} NMR resonances of complexes **2**−**8** and **10** appear at δ −32.9 to −35.2, while the phosphorus nucleus for the sterically bulky mesityl complex **9** resonates further upfield at δ −43.9. These complexes absorb at 1997−2035 cm^{-1} (ν_{CO}) in their infrared spectra. These stretching frequencies are normal for terminal carbon monoxide ligands.[21]

A single-crystal X-ray diffraction study was performed on mesityl complex **9**. Colorless block-shaped crystals were grown by vapor diffusion of pentane into a dichloromethane solution of **9** at −35 °C over 1 week. Details of the solution of the structure are given in the Experimental Section. The cationic portion of **9** was disordered; successful modeling of the data was achieved with 5% occupancy of Ir(2) and P(2). The bonding and molecular geometry of the major component of the cationic portion of **9** are illustrated in Figure 1. The Ir(1)−C(2) (mesityl ligand) bond length was found to be 2.154(5) Å, the Ir(1)−P(1) bond length is 2.333(1) Å, the Ir(1)−C(1) (carbonyl ligand) is 1.860(5) Å, and the Ir(1)−Cp* (centroid) bond length is 1.9018(2) Å. All of these bond lengths are normal. The data collection and refinement parameters are listed in the Experimental Section in Table 4, and a listing of selected bond distances and angles is located in Table 1.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for [Cp*(PMe_3)Ir(mesityl)(CO)][OTf] (9)

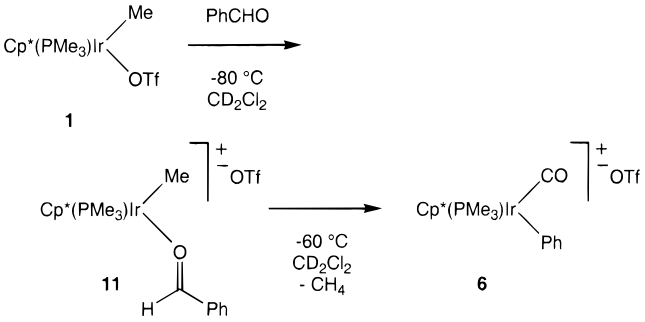
(a) Bond Distances

Ir(1)−C(1)	1.860(5)	Ir(1)−C(14)	2.262(4)
Ir(1)−C(2)	2.154(5)	Ir(1)−C(15)	2.316(5)
Ir(1)−P(1)	2.333(1)	Ir(1)−C(16)	2.298(5)
Ir(1)−Cp* centroid	1.9018(2)	Ir(1)−C(17)	2.246(4)
C(1)−O(1)	1.149(6)	Ir(1)−C(18)	2.253(4)

(b) Bond Angles

P(1)−Ir(1)−C(1)	84.8(2)	C(2)−Ir(1)−Cp* centroid	123.5(1)
P(1)−Ir(1)−C(2)	92.4(1)	P(1)−Ir(1)−Cp* centroid	130.15(3)
C(1)−Ir(1)−C(2)	92.4(2)		

Scheme 1



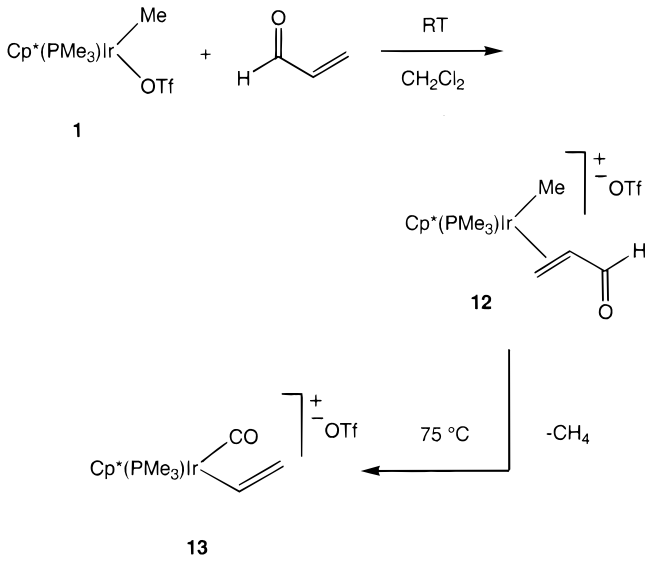
The reactions between **1** and aldehydes are extremely rapid and clean. Monitoring these reactions at room temperature by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy revealed no intermediates or side products; however, monitoring the reaction between benzaldehyde and **1** at low temperature allowed for direct observation of a new species. Benzaldehyde (R = Ph) and a dichloromethane-d_2 solution of **1** were combined at −78 °C in an NMR tube, and the tube was placed in a precooled (−80 °C) NMR spectrometer probe. Monitoring the reaction mixture spectroscopically showed the formation of a new complex. This complex is assigned as the η^1-(O)-bound aldehyde adduct[22] (**11**) of **1** (Scheme 1), on the basis of the ^{1}H and ^{31}P{^{1}H} NMR spectroscopic data; a new aldehyde resonance was observed in the ^{1}H NMR spectrum at 9.50 ppm (cf. δ 10.01 for free benzaldehyde). This small change in the aldehydic proton resonance is typical of η^1(O)-bound aldehyde adducts. The aldehydic proton resonance for adducts that are π-bound are typically shifted farther upfield (6−7 ppm).[23] The new aldehydic proton resonance was accompanied by new resonances for the metal-bound Cp* ligand, the trimethylphosphine ligand, and the iridium-bound methyl group. When the probe of the NMR spectrometer was warmed to −60 °C, the resonances for **11** disappeared ($t_{1/2} \approx$ 10 min) and were replaced by resonances corresponding to **6** and methane.

(21) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 110−117.

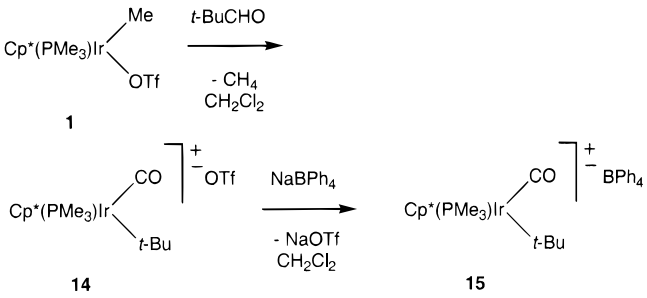
(22) Aldehydes are known to bind to transition metals η^1 through oxygen[23,27−29] and η^2 through the C=O double bond.[23,27−30]

(23) Lenges, C. P.; Brookhart, M.; White, P. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 552−555.

Scheme 2



Scheme 3



To confirm that the methane byproduct produced in the reactions of **1** with aldehydes is a result of activation of the aldehydic C−H bond, the reaction of **1** with acetaldehyde-1-*d* (eq 2) was investigated. This produced

$$\underset{\mathbf{1}}{\mathrm{Cp^*(PMe_3)Ir(Me)(OTf)}} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{CH_3CDO}} \underset{\mathbf{2}}{\mathrm{[Cp(PMe_3)Ir(Me)(CO)][OTf]}} + \mathrm{CH_3D} \quad (2)$$

exclusively CH_3D (no CH_4 was observed) and **2** (determined by ^{1}H NMR spectroscopy). This experiment also eliminates the possibility that C−H activation in these reactions proceeds through a cyclometalated intermediate, as has been suggested[24,25] and ruled out in other studies as well.[26]

Addition of acrolein (CH_2=CHCHO) to a CD_2Cl_2 solution of **1** at room temperature did not directly form the expected vinyl carbonyl complex (**13**) (Scheme 2). Instead, coordination of acrolein to iridium starting material **1** produced π-complex **12** in 63% isolated yield. A new aldehydic proton resonance is observed in the ^{1}H NMR spectrum of **12** at δ 8.23 (cf. δ 9.55 for free acrolein). It appears as a broad doublet, and the resonance for the carbon atom of the carbonyl moiety appears at δ 191.9 (cf. δ 194.4 for free acrolein). Additionally, the alkene resonances in the ^{1}H and ^{13}C-{^{1}H} NMR spectrum are shifted significantly upfield relative to those of free acrolein. These data suggest that **12** is an alkene adduct, not a carbonyl (either η^1 or η^2) adduct.[23,27−31] In agreement with this formulation, coupling is also observed in complex **12** between all three vinylic protons and the iridium-bound phosphorus atom, and **12** exhibits a strong carbonyl stretch in the infrared spectrum at ν_{CO} 1677 cm^{-1}. Finally, the ^{1}H NMR spectrum of **12** exhibits a signal for the iridium-bound methyl group which appears as a doublet ($^3J_{P-H}$ = 6.4 Hz) at 0.81 ppm (cf. 0.92 ppm for **1**), indicating that loss of methane has not occurred. Complex **12** was found to be the kinetic product of the reaction, as subsequent thermolysis in CD_2Cl_2 (75 °C, 24 h) afforded the expected vinyl carbonyl product **13** in 57% isolated yield (Scheme 2). Vinyl complex **13** shows no unusual spectroscopic features.

Synthesis of Tertiary Alkyl Substituted Iridium Complexes. The general reaction sequence illustrated in eq 1 also provides a synthetic route to tertiary alkyl complexes of iridium. For example, addition of 1 equiv of 2,2-dimethylpropanal (*t*-BuCHO) to **1** provided the *tert*-butyl carbonyl triflate salt **14** (Scheme 3). Multiple attempts to grow crystals suitable for X-ray diffraction were unsuccessful. Therefore, we decided to exchange the triflate anion for an anion of increased crystallinity. Subjecting **14** to anion metathesis using sodium tetraphenylborate cleanly afforded [Cp*(PMe$_3$)Ir(*t*-Bu)(CO)][BPh$_4$] (**15**).

An X-ray diffraction study of **15** was undertaken, since we were aware of no isolated iridium complexes bearing tertiary alkyl ligands. Pale columnar crystals of **15** were grown from a toluene/CH_2Cl_2 solution at −30 °C over 2 weeks. The bonding and molecular geometry of the major component of the cationic portion of **15** is illustrated in Figure 2. Solution of the structure was complicated by substantial disorder and twinning. Details of the structure analysis are given in the Experimental Section. Although the nondisordered molecule shows the expected three-legged piano-stool coordination geometry, care should be exercised in the interpretation of the geometric data. The data collection and refinement parameters are provided in Table 4, and a listing of selected bond distances and angles is located in Table 2.

Adamantane-1-carboxaldehyde (**16**), prepared from adamantylmethanol via a Swern oxidation[32] in 59% yield, reacts cleanly with **1** to give the 1-adamantyl triflate salt **17** (Scheme 4) in 72% isolated yield. Because of the difficulty in growing X-ray-quality crystals, we again decided to exchange the triflate anion for another anion, this time using BAr$_f$. Anion metathesis was performed by the addition of NaBAr$_f$ to **17** in dichlo-

(24) Hinderling, C.; Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1997**, *119*, 10793−10804.
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(32) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165−185.

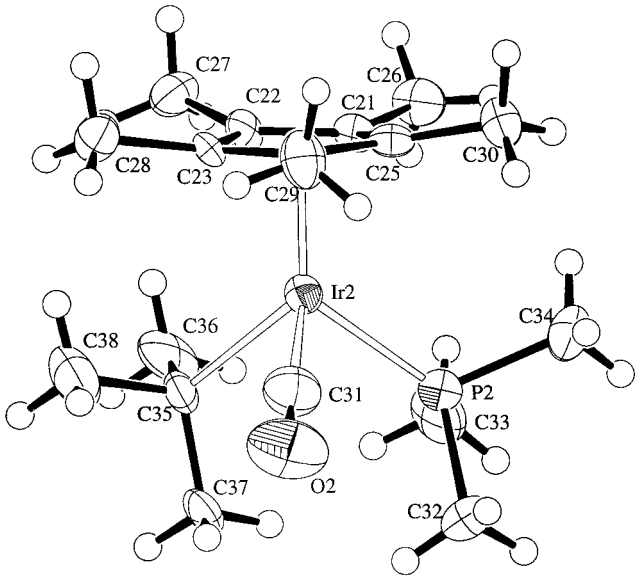


Figure 2. ORTEP plot of the solid-state molecular structure of the major component of the cationic portion of [Cp*-(PMe_3)Ir(*t*-Bu)(CO)][BPh_4] (**15**). Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [Cp*(PMe_3)Ir(*tert*-butyl)(CO)][BPh_4] (15)

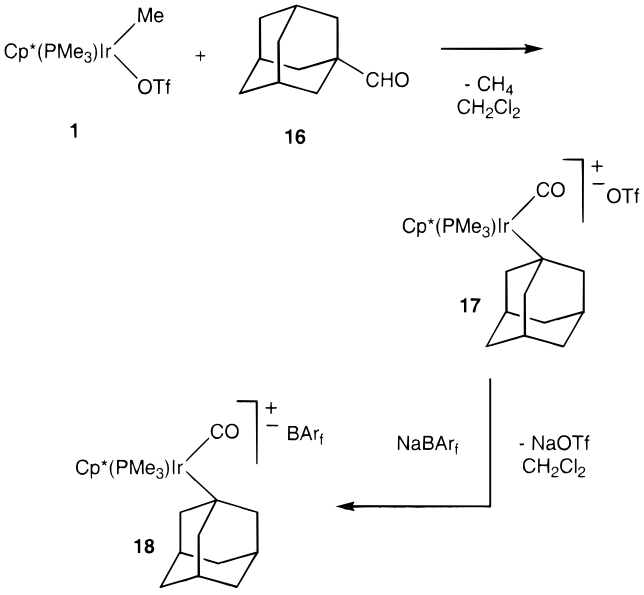
(a) Bond Distances

Ir(2)−P(2)	2.317(2)	Ir(2)−C(21)	2.270(7)
Ir(2)−C(35)	2.215(6)	Ir(2)−C(22)	2.328(7)
Ir(2)−C(31)	1.837(9)	Ir(2)−C(23)	2.256(7)
O(2)−C(31)	1.155(8)	Ir(2)−C(24)	2.271(7)
Ir(2)−Cp* centroid	1.9466(6)	Ir(2)−C(25)	2.308(7)

(b) Bond Angles

Ir(2)−C(31)−O(2)	176.5(7)	C(35)−Ir(2)−Cp* centroid	126.2(2)
P(2)−Ir(2)−C(31)	90.9(2)	C(31)−Ir(2)−Cp* centroid	125.6(3)
P(2)−Ir(2)−C(35)	92.3(2)	P(2)−Ir(2)−Cp* centroid	125.37(9)
C(31)−Ir(2)−C(35)	84.6(3)		

Scheme 4



romethane to give [Cp*(PMe_3)Ir(1-adamantyl)(CO)]-[BAr_f] (**18**) in 99% yield.

A single-crystal X-ray diffraction study of the 1-adamantyl-substituted complex **18** was undertaken due to the disorder and twinning in the structure of *tert*-butyl

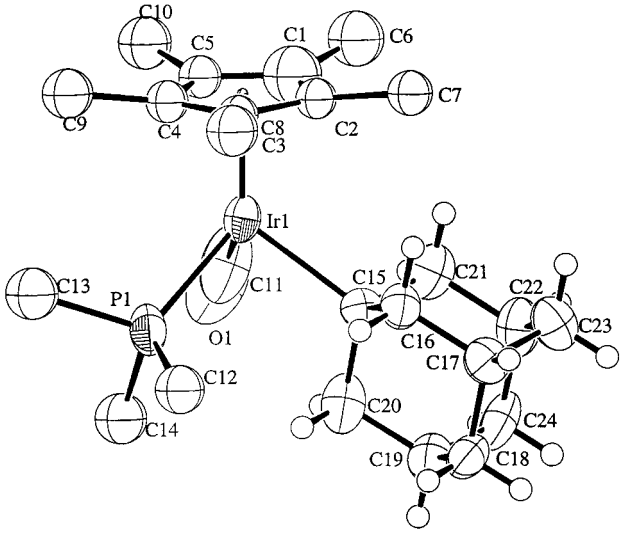


Figure 3. ORTEP plot of the solid-state molecular structure of the major component of the cationic portion of [Cp*-(PMe_3)Ir(1-adamantyl)(CO)][BAr_f] (**18**). Thermal ellipsoids are shown at the 50% probability level. Some of the hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for [Cp*(PMe_3)Ir(1-adamantyl)(CO)][BAr_f] (18)

(a) Bond Distances

Ir(1)−P(1)	2.342(5)	Ir(1)−;C(1)	2.349(7)
Ir(1)−C(15)	2.27(1)	Ir(1)−C(2)	2.337(6)
Ir(1)−C(11)	1.78(1)	Ir(1)−C(3)	2.287(6)
O(1)−C(11)	1.11(2)	Ir(1)−C(4)	2.268(7)
Ir(1)−Cp* centroid	1.977(1)	Ir(1)−C(5)	2.308(7)

(b) Bond Angles

Ir(1)−C(11)−O(1)	173(1)	C(15)−Ir(1)−Cp* centroid	124.4(3)
P(1)−Ir(1)−C(11)	85.4(6)	C(11)−Ir(1)−Cp* centroid	127.6(5)
P(1)−Ir(1)−C(15)	92.1(3)	P(1)−Ir(1)−Cp* centroid	128.1(1)
C(11)−Ir(1)−C(15)	86.3(6)		

complex **15**. Pale yellow bladelike crystals of **18** were grown from a toluene/CH_2Cl_2 solution at −30 °C over 1 week. Complex **18** crystallized in the space group *C*2/*c* (No. 15) with eight cation/anion pairs and a toluene of solvation in the unit cell. The data collection and refinement parameters are provided in the Experimental Section in Table 4. The bonding and molecular geometry of the major component of the cationic portion of **18** are illustrated in Figure 3. The structure clearly shows that the molecule has a standard three-legged piano-stool geometry, with the 1-adamantyl ligand *σ*-bonded to the iridium atom. Unfortunately, the cationic portion of **18** displayed substantial disorder in the structure. The details of the structure solution and refinement are given in the Experimental Section. A listing of selected bond distances and angles is located in Table 3; these data should be interpreted with care due to the disorder in the structure.

Reactivity of Selected Cationic Hydrocarbyl Carbonyl Complexes: Decarbonylation and Attempted Carbonylation Reactions. The products of the reactions discussed above may be further elaborated. Photolysis of a sample of phenyl carbonyl complex **6** in a sealed Pyrex NMR tube resulted in decarbonylation.[33] In a sealed vessel without an added trap, an apparent

(33) We also performed thermal decarbonylation reactions of several complexes using trimethylamine *N*-oxide; however, these reactions were less clean than the photoinitiated reactions.

photostationary state was established between **6** and $Cp^*(PMe_3)Ir(Ph)(OTf)$ (**19**) in CD_2Cl_2 solution (eq 3).

$$[Cp^*(PMe_3)Ir(Ph)(CO)][OTf] \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \underset{\mathbf{19}}{Cp^*(PMe_3)Ir(Ph)(OTf)} + CO \quad (3)$$
$$\mathbf{6}$$

Upon standing overnight in ambient room light, the $Cp^*(PMe_3)Ir(Ph)(OTf)$ (**19**) generated by the photolysis reacted with the liberated CO to re-form starting material **6**. When a similar photolysis of methyl derivative **2** was performed in the presence of trimethylphosphine (10-fold excess), added to act as a trap for **1**, $[Cp^*(PMe_3)_2Ir(Me)][OTf]$ (**20**) was formed in 42% yield (vs trimethoxybenzene internal standard) (eq 4). Com-

$$[Cp^*(PMe_3)Ir(Me)(CO)][OTf] \xrightarrow[CD_2Cl_2]{h\nu,\ PMe_3} \underset{\mathbf{20}}{[Cp^*(PMe_3)_2Ir(Me)][OTf]} + CO \quad (4)$$
$$\mathbf{2}$$

plex **20** was synthesized independently by addition of PMe_3 to **1**; details are given in the Experimental Section.

Photolysis of cyclopropyl complex **5** under the reaction conditions described above gave a somewhat different result. In the absence of an added trap, the reaction afforded $[Cp^*(PMe_3)Ir(\eta^3\text{-allyl})][OTf]$ (**21**) (eq 5). This

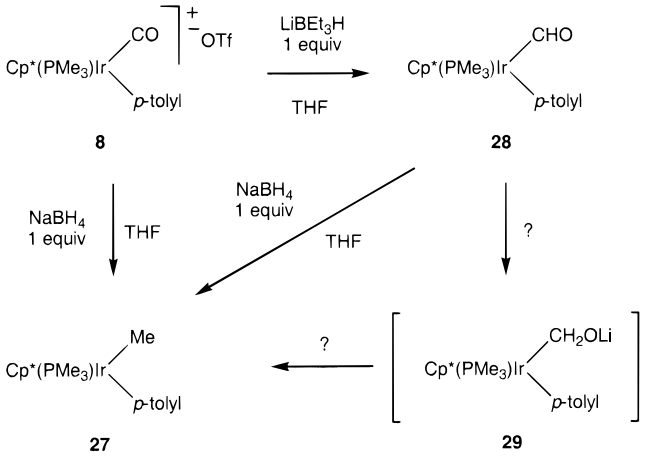
$$[Cp^*(PMe_3)Ir(c\text{-}Pr)(CO)][OTf] \xrightarrow[CD_2Cl_2]{h\nu} \underset{\mathbf{21}}{[Cp^*(PMe_3)Ir(\eta^3\text{-allyl})][OTf]} + CO \quad (5)$$
$$\mathbf{5}$$

complex was presumably formed via the cyclopropyl complex $Cp^*(PMe_3)Ir(c\text{-}Pr)(OTf)$ by β-alkyl elimination (see Discussion). When the photolysis was instead performed in the presence of a trap such as PMe_3 (in 10-fold excess), or in neat CH_3CN, formation of an intractable mixture of complexes resulted. Thus, intermolecular trapping of the decarbonylated intermediate "$Cp^*(PMe_3)Ir(c\text{-}Pr)$" to form $[Cp^*(PMe_3)Ir(c\text{-}Pr)(L)][OTf]$ (L = PMe_3, CH_3CN) (**22**) could not be cleanly effected.

The β-alkyl elimination (ring-opening) reaction observed in the photolysis of cyclopropyl complex **5** prompted us to investigate whether clean β-hydride elimination reactions could be induced in any of our tertiary alkyl complexes. Photolysis of *tert*-butyl-substituted complex **14** in CD_2Cl_2 did not yield the isobutylene hydride complex $[Cp^*(PMe_3)Ir(H)(CH_2{=}CMe_2)][OTf]$ (**23**) cleanly. Although a single metal hydride resonance and new olefinic resonances were observed in the ^1H NMR spectrum, five different sets of resonances for the Cp* and PMe_3 ligands were also present. Similarly, photolysis of 1-adamantyl salt **17** afforded only intractable mixtures of products.

Further derivatization of the hydrocarbyl carbonyl complexes **2**−**10** could conceivably be effected via their carbonylation. However, thermolysis (105 °C) of methyl and phenyl carbonyl complexes **2** and **6** under 1 atm of carbon monoxide did not give the corresponding acyl carbonyl complexes $[Cp^*(PMe_3)Ir(COR)(CO)][OTf]$ (R = Me, **24**; R = Ph, **25**). Furthermore, subjection of **2** to more forcing conditions (10 atm CO, 135 °C) also did not afford **24**. Since it was unclear whether these reactions were unsuccessful due to kinetic or thermodynamic concerns, two additional experiments were performed. In the first experiment, variable-temperature NMR spectroscopy on the high-pressure (10 atm) sample was used to determine whether any acyl carbonyl complex **24** was formed at high temperature, which upon cooling to room temperature rapidly returned to a mixture of **2** and carbon monoxide. NMR spectra (^1H and $^{31}P\{^1H\}$) of this reaction obtained between 20 and 100 °C showed no additional resonances, providing no evidence for this hypothesis. In our second experiment, we attempted to synthesize $Cp^*(PMe_3)Ir(COMe)(Cl)$ by addition of [PPN][Cl] to a CD_2Cl_2 solution of **2**. This also failed to cleanly produce a new acyl−iridium complex.

Scheme 5



Carbonyl Reduction Reactions.[34−36] Addition of excess $NaBH_4$ or $LiAlH_4$ to methyl carbonyl complex **2** resulted in the complete reduction of the CO ligand to a methyl group, leading to complex **26** (eq 6). Similarly,

$$[Cp^*(PMe_3)Ir(Me)(CO)][OTf] \xrightarrow[THF]{NaBH_4 \text{ or } LiAlH_4} \underset{\mathbf{26}}{Cp^*(PMe_3)IrMe_2} \quad (6)$$
$$\mathbf{2}$$

$Cp^*(PMe_3)Ir(p\text{-tolyl})(Me)$ (**27**) was synthesized by addition of excess $NaBH_4$ to **8** (Scheme 5). Spectroscopic data for $Cp^*(PMe_3)Ir(Me)_2$ (**26**)[37] and $Cp^*(PMe_3)Ir(p\text{-tolyl})(Me)$ (**27**)[38] are in excellent agreement with the values reported in the literature. Interestingly, we have been able to isolate one of the compounds that is presumably an intermediate on the CO-to-methyl reduction pathway for complex **8**, formyl (IrCHO) complex **28** (Scheme 5).[39−49] Careful addition of 1 equiv of $LiBEt_3H$ to **8** gave **28** in 84% yield. The ^1H NMR

(34) Reduction of transition-metal carbonyl ligands to formyl, hydroxymethyl, and methyl ligands has been observed before. For leading references, see refs 35−36.

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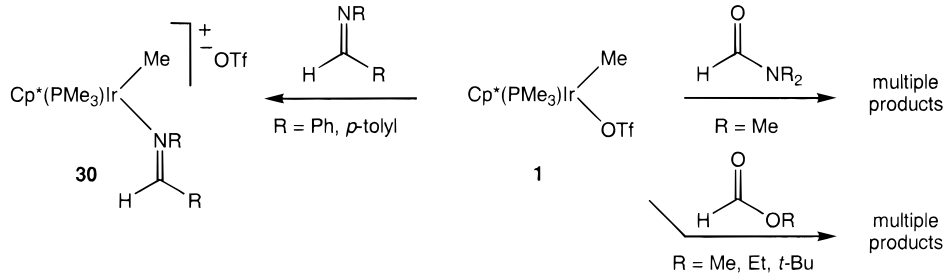
(39) The scarcity of reported formyl and hydroxymethyl complexes synthesized by reduction of a CO ligand is due to the ease by which these complexes undergo further reduction. For recent examples of transition-metal formyl complexes see refs 40−49.

(40) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1−38.

Scheme 6



spectrum of **28** contains a resonance at δ 13.97 (IrC*H*O), and the $^{13}C\{^1H\}$ NMR spectrum contains a broad formyl carbon resonance at δ 231.6 that was positive in a DEPT 90 experiment. These chemical shift values are not unusual for transition-metal formyl complexes.[40] Although addition of 2 equiv of $LiBEt_3H$ to **8** should give the lithiated hydroxymethyl complex ($IrCH_2OLi$) **29** (Scheme 5), we were unsuccessful in isolating this complex.

Reactions of 1 with Other Organic Molecules That Contain the −CHE (E = O, NR) Moiety. The addition of aldimines, formates, or formamides to **1** yielded no isolable examples of the alkyl isocyanide, alkoxy carbonyl, or amido carbonyl complexes (Scheme 6) that might be anticipated by analogy to the reaction of **1** with aldehydes. Instead, apparent adduct formation occurred with aldimines,[50−52] and intractable product mixtures resulted from reaction of **1** with formates or formamides. Addition of 1.5 equiv of aldimines (RN=CRH, R = Ph, *p*-tolyl) to **1** resulted in rapid formation of one major product (**30**; Scheme 6) and several minor products (determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy). The ^1H NMR spectrum of the major component of the reaction mixture contained new resonances for the Cp* ligand (R = Ph, 1.71 ppm; R = *p*-tolyl, 1.69 ppm), the PMe_3 ligand (R = Ph, 1.27 ppm; R = *p*-tolyl, 1.29 ppm), and the Ir−Me moiety (R = Ph, 0.58 ppm; R = *p*-tolyl, 0.50 ppm) as well as new aryl resonances. A new aldimine (RN=CR*H*) proton was also visible at 8.46 ppm (R = Ph) and 8.17 ppm (R = *p*-tolyl). The major resonance in the $^{31}P\{^1H\}$ NMR spectrum appeared at −34.2 ppm (R = Ph) and −32.0 ppm (R = *p*-tolyl). From these data and the absence of any resonances indicative of the formation of either methane or a new iridium hydride, we conclude that no C−H activation has occurred. Purification of these complexes by recrystallization from CH_2Cl_2 or chromatography (air-free) on dried silica, alumina I, or alumina III was unsuccessful. Addition of *N*,*N*-dimethylformamide (Me_2NCHO) (1.5 equiv) to **1** gave two major and more than seven minor products that could also not be purified. Addition of alkyl-substituted formates (ROCHO; R = Me, Et, *t*-Bu) (1.5 equiv) gave mixtures of three to five reaction products that also could not be purified by repeated crystallization attempts.

Discussion

Activation of Aldehyde C−H Bonds. The activation of the aldehydic C−H bond has been observed in several other laboratories, occurring with iron(0),[53] ruthenium(0),[54,55] ruthenium(II),[56] osmium(0),[57−59] rhodium(I),[60−66] rhodium(III),[67] iridium(I),[66,68−73] iridium(III),[67] and platinum(0).[74] In some cases, the C−H activation step is followed by decarbonylation of the metal−acyl intermediate;[55,56,67−70,74] in others an acyl hydride complex is the stable product of the reaction.[57,58,66,74] The only published example to date of

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(51) Faller, J. W.; Ma, Y.; Smart, C. J.; DiVerdi, M. J. *J. Organomet. Chem.* **1991**, *420*, 237−252.
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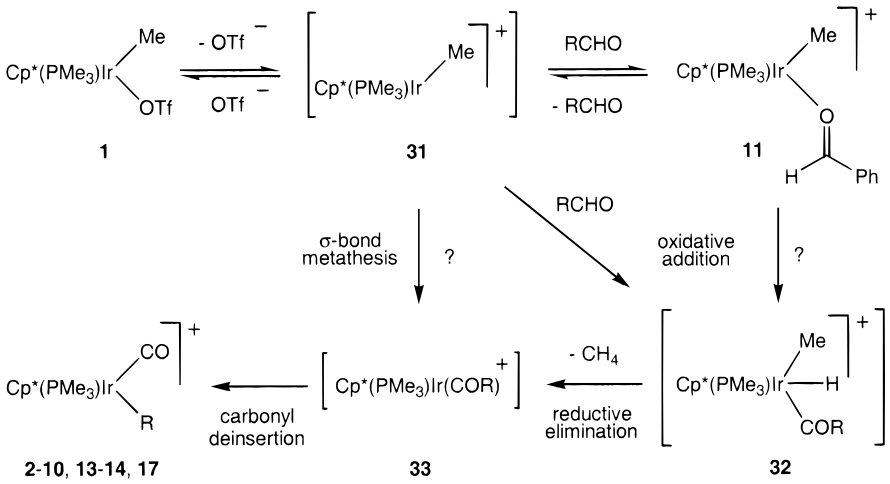
Scheme 7



aldehydic C−H bond activation by an iridium(III) complex was reported in 1985.[67] In that study, Maitlis and co-workers found that the neutral complexes Cp*M-$(Me)_2$(DMSO) (M = Rh, Ir) reacted with aldehydes in cyclohexane solution at 80 °C over several (4−24) hours.

Much of the activity in this area has been focused on demonstrating the intermediacy of acyl hydride complexes in processes such as the metal-catalyzed carbonylation of C−H bonds,[75,76] hydroformylation of olefins,[76−79] and decarbonylation reactions of aldehydes.[76,80−82] The majority of the research on aldehyde decarbonylation has utilized Rh(I) complexes as catalysts,[83−91] since these have been found to be most efficient; however, some systems utilizing Pd/C,[92] ruthenium(II),[93] cobalt(I),[94] cobalt(II),[95,96] iridium(I),[69,70] and scandium(III)[97] complexes have also been successful.

Selectivity of C−H Activation. Earlier researchers in our group primarily investigated the activation of organic substrates that contained only one type of C−H bond (e.g., methane, benzene, cyclopropane, acetone).[14,15,17] Since then, our studies have focused on the selectivity displayed in reactions between **1** and organic substrates which present a variety of C−H bond types (i.e., primary, secondary, aromatic, benzylic, etc.).[18,20] One important goal of the work presented here was to further examine the degree of selectivity of the highly reactive reagent **1**. Despite the fact that the activation of aldehydes by **1** is usually complete within 1 min at room temperature, and at rapid rates at temperatures as low as −60 °C, the reactions of **1** with aldehydes proceed with a very high degree of selectivity. In most cases only a single product is observed by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy. High yields (quantitative by NMR spectroscopy, 63−87% following recrystallization or precipitation) of the iridium(III) hydrocarbyl carbonyl cations **2**−**10**, **13**, **14**, and **17** are obtained, and there is no evidence for activation of any C−H bond other than the aldehydic one.

Proposed Mechanism of C−H Activation and Subsequent Rearrangements. On the basis of our previous studies of complex **1** and its related BAr_f salt ($[Cp^*(PMe_3)IrMe(CH_2Cl_2)][BAr_f]$) we postulate that these C−H activation reactions proceed through coordinatively unsaturated cationic species **31** (Scheme 7).[14−16] Although we have observed benzaldehyde adduct **11** at −80 °C by NMR spectroscopy, it is unclear whether **11** is an intermediate on the reaction pathway or simply a kinetic "dead end" formed reversibly from **31**. One mechanistic possibility is that the C−H activation step occurs via an iridium(V) intermediate such as **32**. This proposed Ir(V) intermediate could form either from aldehyde adduct **11** or by an intermolecular pathway (from **31** and aldehyde). While kinetics experiments designed to distinguish between these pathways were attempted, the reactions were too rapid to obtain high-

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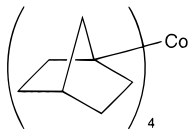
quality data using conventional kinetics techniques. Reductive elimination of methane from acyl hydride **32** would form the coordinatively unsaturated acyl complex **33**, and migratory deinsertion of CO from **33** would give the observed product. Alternatively, the C−H activation could occur by a concerted σ-bond metathesis reaction; however, we disfavor this mechanistic possibility based on prior research.[98−100]

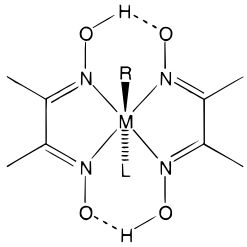
Synthesis of Unusual Alkyl Complexes of Iridium. One of the most notable features of this chemistry is the fact that even when the alkyl group on the aldehyde is tertiary, the reaction still proceeds to give an Ir(tertiary alkyl) product. The migratory CO deinsertion reaction proposed above occurs readily, in spite of the fact that it brings sterically demanding groups (mesityl, *tert*-butyl, 1-adamantyl) in close proximity to the metal center. Acyl species **33** could conceivably achieve coordinative and electronic saturation by coordination of the acyl oxygen atom to the iridium to form a stable η^2-acyl complex. Instead, even with very hindered groups, the deinsertion reaction occurs. We believe this process is likely driven in large part by the high M−CO bond energy.

The first syntheses of transition-metal complexes containing tertiary alkyl ligands were reported in 1972.[101−103] Since then, very few tertiary alkyl complexes of any of the transition metals have been described.[104−116] Such complexes have been difficult to isolate, due to their propensity to decompose to stable transition-metal hydrides via further reactions such as β-elimination.[117] Most of the stable transition-metal tertiary alkyl complexes are either coordinatively saturated, and thus have a very high barrier to β-elimination, or are stable because upon undergoing β-elimination they would form thermodynamically unstable bridgehead alkenes. In group 9, we are aware of a few isolated tertiary alkyl complexes of cobalt[118−125] and rhodium[126] (Chart 1) but none of iridium.[127,128] To the best of our knowledge, *tert*-butyl and 1-adamantyl salts **14**, **15** and **17**, **18** are the first such reported complexes.

Chart 1. Complete List of Previously Reported Group 9 Tertiary Alkyl Complexes



Bower, 1972
Theopold, 1986



M = Co
- R = 1-methyl-2,2-diphenylcyclopropyl
  - L = pyridine; Jensen, 1973
- R = 1-norbornyl
  - L = pyridine; Eckert, 1977
- R = 1-adamantyl
  - L = pyridine; Eckert, 1977
  - L = 1-methylimidazole; Marzilli, Randaccio, 1984
  - L = 1,5,6-trimethylbenzimidazole; Attia, 1984
  - L = $P(OMe)_3$, $P(O\textit{i}\text{-}Pr)_3$; Randaccio, Marzilli, 1985
  - L = NH_2Ph, *p*-(NMe_2)pyridine; Randaccio, 1989
  - L = H_2O, PPh_2Et; Randaccio, 1992

M = Rh
- R = *t*-butyl
  - L = 4-*t*-butylpyridine; Giese, Hartung, 1993

This methodology has also allowed for the synthesis of cyclopropyl derivative **5**. Though few cyclopropyl-substituted transition-metal complexes have been reported, most of those that are known have been prepared by one of two general methods: Grignard (or Grignard-like) substitutions of metal halides[129−133] and

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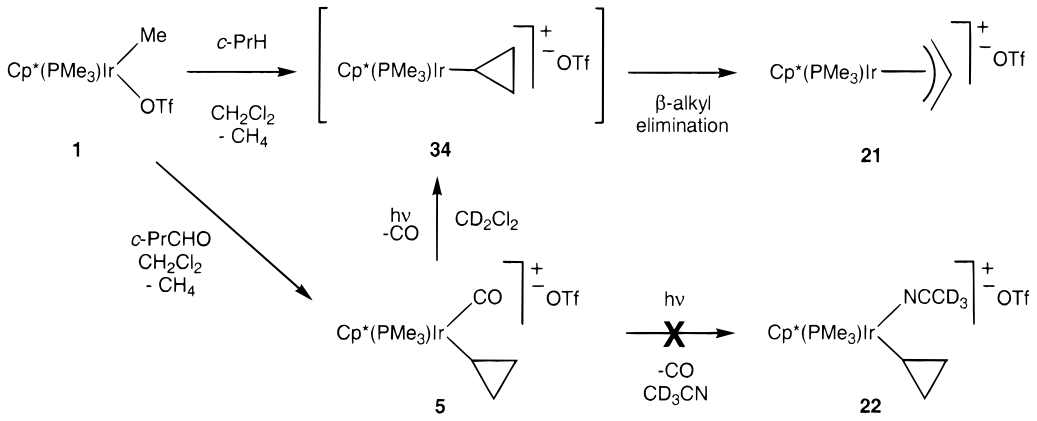
Scheme 8



C−H activation of cyclopropane by the transiently generated Cp′(PMe$_3$)M (Cp′ = Cp, Cp*; M = Rh, Ir) fragment.[128,134−139]

We feel that our ability to access these unusual organometallic compounds is intimately linked to the tandem nature of the C−H activation/decarbonylation steps and the resulting absence of a coordinatively unsaturated *alkyl* complex on the reaction pathway. In the aldehyde C−H activation reaction, we propose that the coordinatively unsaturated *acyl* complexes (**33**) proposed as intermediates undergo rearrangement by a carbonyl migratory deinsertion reaction to directly form 18-electron hydrocarbyl carbonyl complexes **2**−**10**, **13**, **14**, and **17**. This reaction sequence allows for the direct alkylation of iridium by the overall transfer of the R group from the aldehyde (RCHO) to the metal without any subsequent rearrangement of the alkyl group. Thus, whereas **1** does *not* react cleanly with tertiary C−H bonds to give stable *tert*-butyl-substituted iridium compounds, reaction of **1** with 2,2-dimethylpropanal proceeds rapidly and cleanly to afford *tert*-butyl complex **14** with no detectable side products. Likewise, reaction of **1** with cyclopropane produces a π-allyl complex, while cyclopropyl-substituted complex **5** can be easily synthesized free of ring-opened products using cyclopropanecarboxaldehyde. In essence, the CO deinsertion reaction serves to protect the alkyl group by filling the coordination site on the metal center.

Elaboration of the Products of the Tandem C−H Activation/Decarbonylation Reactions. To demonstrate additional utility of the tandem reaction described above for the synthesis of novel iridium alkyl complexes, we sought to elaborate complexes **2**−**10**, **13**, **14**, and **17**. We explored decarbonylation, carbonylation, and carbonyl reduction reactions of these molecules.

Decarbonylation of transition-metal carbonyl complexes has been used to perform ligand substitution[140] and rearrangement reactions.[141] In this study, we have utilized this reaction to gain further evidence about the putative intermediate in the reaction between **1** and cyclopropane. Treatment of **1** with cyclopropane results in the formation of methane (1 equiv) and π-allyl complex [Cp*(PMe$_3$)Ir(η^3-allyl)][OTf] (**21**) (Scheme 8).[15] We assume that C−H activation affords a coordinatively unsaturated cyclopropyl complex (**34**), although we have never observed such an intermediate directly. We therefore postulate that this intermediate undergoes rapid ring opening by a kinetically facile β-alkyl elimination reaction to produce the observed product.[142] It occurred to us that photochemically induced decarbonylation of the cyclopropyl carbonyl complex (**5**) would provide an alternate route to **34**. The observation of π-allyl complex [Cp*(PMe$_3$)Ir(η^3-allyl)][OTf] (**21**) as the reaction product in the decarbonylation of **5** lends further support to our proposal involving coordinatively unsaturated cyclopropyl intermediate **34**.[143−145]

The success of the β-alkyl elimination reaction of **5** prompted us to attempt to induce β-hydride elimination from *tert*-butyl complex **14** and 1-adamantyl complex **17**. Decarbonylation followed by β-hydride elimination from **14** or **17** would result in the formation of isobutylene hydride **23** or adamantene hydride complex **35**, respectively. Of particular interest to us was the decarbonylation of **17**, as it presented a possible method for forming metal-stabilized highly strained anti-Bredt bridgehead alkenes.[146−152] Unfortunately, we were not able to cleanly promote β-hydride elimination from

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(143) As a reviewer has pointed out, the conversion of a transition-metal σ-cyclopropyl complex to an η^3-allyl complex has been observed in other laboratories. In 1978, Phillips and Puddephatt showed that *trans*-[Pt(c-Pr)Cl(PMe$_2$Ph)$_2$] reacts with Ag(NO$_3$) in the presence of KPF$_6$ to produce [Pt(η^3-C$_3$H$_5$)(PMe$_2$Ph)$_2$][PF$_6$]. They demonstrated that this reaction occurs by cleavage of the β-C−C bond via a deuterium labeling study.[144] A similar reaction was reported by Lehmkuhl and co-workers.[145]
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(146) For examples of strained organic molecules that are stabilized by coordination to transition-metal fragments, see refs 147−152.

either **14** or **17** by photoinduced decarbonylation. This lack of clean reactivity provides further support for the tandem nature of the reactions between **1** and aldehydes.

In our proposed mechanism, acyl intermediate **33** undergoes a carbonyl migratory deinsertion reaction (Scheme 7). Many groups have studied the mechanism of this reaction type with a variety of complexes.[153−155] The carbonylation of methyl carbonyl complex **2** was attempted to test whether this step is reversible. However, even under 10 atm of CO pressure, **2** does not react to form acetyl carbonyl complex **24**. At the present time, it is unclear whether (a) the migratory deinsertion step is irreversible, (b) trapping of the acyl intermediate with exogenous CO is kinetically incompetent, or (c) complex **24** lies thermodynamically uphill relative to **2** and CO.

Conclusion

The tandem C−H activation/carbonyl migratory deinsertion reaction described in this work has provided access to complexes, including tertiary alkyl and cyclopropyl substituted complexes, that are not easily synthesized by other routes. We feel that the success of this synthetic method is a direct consequence of the tandem nature of the reaction mechanism. The photochemically initiated decarbonylation of cyclopropyl carbonyl complex **5** has provided supporting evidence for the occurrence of β-alkyl elimination in the proposed intermediate **34** formed by cyclopropane C−H activation. Further efforts in our laboratory toward utilizing Cp*(PMe$_3$)Ir(Me)OTf (**1**) for the synthesis of other unusual organometallic complexes are in progress.

Experimental Section

General Procedures. Unless otherwise noted, reactions and manipulations were performed at 23 °C in an inert-atmosphere (N_2) glovebox, or using standard Schlenk and high-vacuum-line techniques. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained at room temperature (except where noted) using Bruker AM 400 MHz or DRX 500 MHz spectrometers. In cases where assignment of $^{13}C\{^1H\}$ NMR resonances from the initial $^{13}C\{^1H\}$ NMR spectrum was ambiguous, resonances were assigned using standard DEPT 45, 90, and/or 135 pulse sequences. Infrared (IR) spectra were recorded using samples prepared as KBr pellets or in a standard solution cell with NaCl windows, and spectral data are reported in wavenumbers (cm^{-1}). Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility, on VT ProSpec, ZAB2-EQ, and 70-FE mass spectrometers. Unless otherwise noted, all FAB MS data were acquired from samples in a methylene chloride/3-nitrobenzyl alcohol matrix. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer 2400 Series II CHNO/S analyzer.

Sealed NMR tubes were prepared by attaching the NMR tube directly to a Kontes high-vacuum stopcock via a Cajon Ultra-Torr reducing union and then flame-sealing on a vacuum line. Reactions with gases and low-boiling liquids involved condensation of a calculated pressure of gas from a bulb of known volume into the reaction vessel at −196 °C. Known volume bulb vacuum transfers were accomplished with a digital MKS Baratron gauge attached to a high-vacuum line.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Potassium bromide (Aldrich), Celite (Aldrich), and silica gel (Merck 60, 230−400) were dried in vacuo at 250 °C for 48 h. Toluene (Fisher) was either distilled from sodium metal under N_2 or passed through a column of activated alumina (type A2, size 12 × 32, Purifry Co.) under nitrogen pressure and sparged with N_2 prior to use.[156] Pentane, hexanes, and benzene (Fisher) were either distilled from purple sodium/benzophenone ketyl under N_2 or passed through a column of activated alumina under nitrogen pressure and sparged with N_2 prior to use.[156] Diethyl ether and tetrahydrofuran (Fisher) were distilled from purple sodium/benzophenone ketyl under N_2 prior to use. Dichloromethane (Fisher) was either distilled from CaH_2 (Aldrich) under N_2 or passed through a column of activated alumina under nitrogen pressure and sparged with N_2 prior to use.[156] Deuterated solvents (Cambridge Isotope Laboratories) were purified by vacuum transfer from the appropriate drying agent (Na/Ph_2CO or CaH_2) prior to use. Trimethylphosphine (Aldrich) was vacuum-transferred from sodium metal prior to use. Aldehydes were purified as follows: all were washed with $NaHCO_3$ to remove traces of the corresponding carboxylic acid;[157] acetaldehyde, acetaldehyde-1-*d*, propionaldehyde, butyraldehyde, cyclopropanecarboxaldehyde, 2-ethylbutanal, benzaldehyde, tolualdehyde, mesitaldehyde, α-methylcinnamaldehyde, pivaldehyde (Aldrich, distilled from 4 Å molecular sieves); acrolein (Aldrich, vacuum transferred from $CaSO_4$). Sodium tetraphenylborate (Aldrich) was dried over 4 Å molecular sieves in $CHCl_3$ and then recrystallized. The following complexes were prepared according to literature proceedures: Cp*(PMe$_3$)Ir(Me)(OTf) (**1**),[15] $NaBAr_f$.[158] Spectroscopic data for Cp*(PMe$_3$)Ir(Ph)(OTf) (**19**),[159] [Cp*(PMe$_3$)Ir(η^3-allyl)][OTf] (**21**),[15] Cp*(PMe$_3$)IrMe$_2$ (**26**),[37] and Cp*(PMe$_3$)Ir(*p*-tolyl)(Me) (**27**)[38] were in accord with literature values.

General Procedure for the Synthesis of [Cp*(PMe$_3$)(Ir(R)(CO)][OTf] (2−10, 14, 17). Synthesis was performed by dissolving iridium triflate **1** in dichloromethane (5 mL) in a 20 mL scintillation vial. The aldehyde was dissolved in dichloromethane (1 mL), and this solution was added to the iridium triflate solution over 1 min. This resulted in vigorous evolution of methane. The mixture was then stirred at room temperature overnight. The volatile materials were then removed in vacuo, and the remaining solids were washed with diethyl ether (to remove excess aldehyde) and purified as described in each specific case below.

[Cp*(PMe$_3$)Ir(Me)(CO)][OTf] (2). Synthesis was performed by employing the general procedure described above using 42.5 mg (0.075 mmol) of **1** and 6.6 mg (0.150 mmol) of ethanal. Complex **2** was isolated (37.6 mg, 0.063 mmol) as a white powder (84% yield) by precipitation from CH_2Cl_2 solution by addition of Et_2O. Mp: >250 °C. ^1H NMR (CD_2Cl_2, 400 MHz): δ 1.97 (d, $^4J_{P-H}$ = 2.1 Hz, 15H, $C_5(CH_3)_5$), 1.69 (d, $^2J_{P-H}$

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= 11.1 Hz, 9H, P(CH_3)$_3$), 0.51 (d, $^3J_{P-H}$ = 6.0 Hz, 3H, IrCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 167.6 (d, $^2J_{P-C}$ = 11.8 Hz, *C*O), 102.0 (s, $C_5(CH_3)_5$), 14.3 (d, $^1J_{P-C}$ = 42.3 Hz, P(*C*H$_3$)$_3$), 8.8 (s, $C_5(CH_3)_5$), −25.6 (d, $^2J_{P-C}$ = 7.0 Hz, Ir*C*H$_3$). ^{19}F NMR (CD_2Cl_2): δ −77.7 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −34.9 (s). IR (CD_2Cl_2): 2035 (s), 1271 (vs). Anal. Calcd for $C_{16}H_{27}F_3IrO_4PS$: C, 32.26; H, 4.57. Found: C, 32.38; H, 4.60.

[Cp*(PMe$_3$)Ir(Et)(CO)][OTf] (3). Synthesis was performed by employing the general procedure described above using 111 mg (0.196 mmol) of **1** and 14.8 mg (0.254 mmol) of propanal. After removal of the volatile materials, **3** was dissolved in 1 mL of CH_2Cl_2 and then precipitated by addition of 3 mL of Et_2O. Compound **3** was isolated (77.0 mg, 0.126 mmol) as a white powder (64% yield). Mp: 249−251 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.02 (d, $^4J_{P-H}$ = 2.4 Hz, 15H, $C_5(CH_3)_5$), 1.75 (d, $^2J_{P-H}$ = 11.2 Hz, 9H, P(CH_3)$_3$), 1.58−1.80 (m, 1H, diastereotopic CH_2CH$_3$), 1.48 (dd, $^3J_{H-H}$ = 7.2 Hz, $^3J_{H-H}$ = 7.2 Hz, 3H, CH$_2$CH_3), 1.27−1.36 (m, 1H, diastereotopic CH_2CH$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 168.3 (d, $^2J_{P-C}$ = 11.8 Hz, *C*O), 102.9 (s, $C_5(CH_3)_5$), 21.7 (s, CH$_2$*C*H$_3$), 15.1 (d, $^1J_{P-C}$ = 40.0 Hz, P(*C*H$_3$)$_3$), 9.3 (s, $C_5(CH_3)_5$), −6.9 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H$_2$CH$_3$). ^{19}F NMR (CD_2Cl_2): δ −76.9 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −34.15 (s). IR (CD_2Cl_2): 1997 (s), 1295 (m), 1259 (s), 1222 (s), 1147 (s), 1031 (s), 954 (s), 638 (m). Anal. Calcd for $C_{17}H_{29}F_3IrO_4PS$: C, 33.49; H, 4.79. Found: C, 33.21; H, 4.56.

[Cp*(PMe$_3$)Ir(*n*-Pr)(CO)][OTf] (4). Synthesis was performed by employing the general procedure described above using 111 mg (0.196 mmol) of **1** and 18.3 mg (0.254 mmol) of butanal. Compound **4** was isolated (96 mg, 0.154 mmol) as a pale yellow powder (79% yield) by precipitation from CH_2Cl_2 solution by addition of pentane. Mp: 148−150 °C dec. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.02 (d, $^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.75 (d, $^2J_{P-H}$ = 10.8 Hz, 9H, P(CH_3)$_3$), 1.48 (m, 2H, CH_2), 1.13 (m, 2H, CH_2), 0.95 (t, $^3J_{H-H}$ = 6.8 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 168.2 (d, $^2J_{P-C}$ = 11.8 Hz, *C*O), 102.8 (s, $C_5(CH_3)_5$), 30.9 (s, *C*H$_2$CH$_3$), 19.8 (s, *C*H$_3$), 15.0 (d, $^1J_{P-C}$ = 50.0 Hz, P(*C*H$_3$)$_3$), 9.3 (s, $C_5(CH_3)_5$), 2.7 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H$_2$CH$_2$CH$_3$). ^{19}F NMR (CD_2Cl_2): δ −76.9 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −33.76 (s). IR (CD_2Cl_2): 2015 (s), 1459 (m), 1384 (m), 1265 (s), 1147 (s), 1031 (s), 956 (m), 638 (m), 516 (m). Anal. Calcd for $C_{18}H_{31}F_3IrO_4PS$: C, 34.66; H, 5.01. Found: C, 34.26; H, 4.81.

[Cp*(PMe$_3$)Ir(c-Pr)(CO)][OTf] (5). Synthesis was performed by employing the general procedure described above using 112 mg (0.198 mmol) of **1** and 18.1 mg (0.258 mmol) of cyclopropanecarboxaldehyde. Compound **5** was isolated (93 mg, 0.150 mmol) as a white powder (76% yield) by precipitation from CH_2Cl_2 solution by addition of pentane. Mp: 205 °C dec. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.04 (d, $^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.81 (d, $^2J_{P-H}$ = 11.2 Hz, 9H, P(CH_3)$_3$), 1.00 (m, 1H, c-C_3H_5), 0.91 (m, 1H, c-C_3H_5), 0.33 (m, 1H, c-C_3H_5), 0.21 (m, 1H, -C_3H_5), 0.13 (m, 1H, c-C_3H_5). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 168.9 (d, $^2J_{P-C}$ = 11.3 Hz, *C*O), 104.8 (s, $C_5(CH_3)_5$), 17.0 (d, $^1J_{P-C}$ = 41.1 Hz, P(*C*H$_3$)$_3$), 11.3 (d, $^3J_{P-C}$ = 1.3 Hz, *C*H$_2$), 10.8 (s, $C_5(CH_3)_5$), 10.2 (d, $^3J_{P-C}$ = 3.3 Hz, *C*H$_2$), −16.4 (d, $^2J_{P-C}$ = 10.4 Hz, *C*H). ^{19}F NMR (CD_2Cl_2): δ −76.97 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −35.21 (s). IR (CD_2Cl_2): 3062 (w), 2989 (w), 2917 (w), 2009 (s), 1492 (w), 1467 (w), 1430 (w), 1384 (w), 1317 (w), 1265 (s), 1145 (s), 1031 (s), 954 (m), 865 (w), 748 (w), 684 (w), 570 (w), 553 (w), 516 (w). Anal. Calcd for $C_{18}H_{29}F_3IrO_4PS$: C, 34.78; H, 4.70. Found: C, 34.88; H, 4.74.

[Cp*(PMe$_3$)Ir(Ph)(CO)][OTf] (6). Synthesis was performed by employing the general procedure described above using 118 mg (0.205 mmol) of **1** and 32.6 mg (0.308 mmol) of benzaldehyde. Compound **6** was isolated (117 mg, 0.178 mmol) as pale yellow crystals (87% yield) by crystallization from CH_2Cl_2/Et_2O. Mp: 222−225 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.10 (m, 5H, Ph), 1.97 (d, $^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.68 (d, $^2J_{P-H}$ = 11.2 Hz, 9H, P(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 169.3 (d, $^2J_{P-C}$ = 12 Hz, *C*O), 141.0 (s, *o*-C_6H_5), 132.1 (s, *p*-C_6H_5), 127.2 (s, *m*-C_6H_5), 124.3 (d, $^2J_{P-C}$ = 10.4 Hz, *i*-C_6H_5), 86.4 (s, $C_5(CH_3)_5$), 17.4 (d, $^1J_{P-C}$ = 42.0 Hz, P(*C*H$_3$)$_3$), 11.1 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −77.0. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −33.0. IR: (CH_2Cl_2) 2927 (w), 2035 (vs), 1276 (vs), 1164 (s), 1039 (s), 643 (m). FAB LRMS: *m*/*z* 509 ([Cp*(PMe$_3$)Ir(Ph)(CO)]$^+$). Anal. Calcd for $C_{21}H_{29}F_3IrO_4PS$: C, 38.35; H, 4.44. Found: C, 38.19; H, 4.46.

[Cp*(PMe$_3$)Ir(1-ethylpropyl)(CO)][OTf] (7). Synthesis was performed employing the general procedure described above using 117 mg (0.206 mmol) of **1** and 22.7 mg (0.227 mmol) of 2-ethylbutanal. Compound **7** was isolated (106 mg, 0.162 mmol) as a pale yellow powder (79% yield) by precipitation from CH_2Cl_2 solution by addition of Et_2O. Mp: 222−225 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.02 (d, $^4J_{P-H}$ = 2.1 Hz, 15H, $C_5(CH_3)_5$), 1.79 (m, 2H, CH_2), 1.78 (d, $^2J_{P-H}$ = 10.8 Hz, 9H, P(CH_3)$_3$), 1.47 (m, 2H, CH_2), 0.95 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3), 0.93 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 169.0 (d, $^2J_{P-C}$ = 12.0 Hz, *C*O), 123.0 (q, $^1J_{C-F}$ = 319 Hz, *C*F$_3$), 105.0 (s, $C_5(CH_3)_5$), 35.8 (s, *C*H$_2$), 24.0 (s, *C*H), 18.3 (s, *C*H$_3$), 17.8 (d, $^1J_{P-C}$ = 37.1 Hz, P(*C*H$_3$)$_3$), 11.3 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −76.7 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −32.94 (s). IR (CD_2Cl_2): 2011 (s), 1269 (s), 1145 (m), 1029 (m), 950 (m), 636 (m). Anal. Calcd for $C_{20}H_{35}F_3IrO_4PS$: C, 36.86; H, 5.41. Found: C, 36.56; H, 5.30.

[Cp*(PMe$_3$)Ir(*p*-tolyl)(CO)][OTf] (8). Synthesis was performed by employing the general procedure described above using 127 mg (0.219 mmol) of **1** and 39.5 mg (0.329 mmol) of *p*-tolualdehyde. Compound **8** was isolated (118 mg, 0.176 mmol) as a pale yellow powder (80% yield) by precipitation from CH_2Cl_2 solution by addition of Et_2O. Mp: 184−185 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.03 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, $C_6H_4CH_3$), 6.92 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, $C_6H_4CH_3$), 2.28 (s, 3H, *p*-CH_3), 1.98 (d, $^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.68 (d, $^2J_{P-H}$ = 11.2 Hz, 9H, P(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 168 (br s, *C*O), 139 (s, *o*-$C_6H_4CH_3$), 135 (s, *p*-$C_6H_4CH_3$), 131 (s, *m*-$C_6H_4CH_3$), 117 (d, $^2J_{P-C}$ = 10.7 Hz, *i*-$C_6H_4CH_3$), 104 (s, $C_5(CH_3)_5$), 20.6 (s, $C_6H_4CH_3$), 16.0 (d, $^1J_{P-C}$ = 40.2 Hz, P(*C*H$_3$)$_3$), 9.6 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −77.0 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −33.07 (s). IR (CD_2Cl_2): 2919 (w), 2017 (s), 1729 (w), 1486 (w), 1270 (s), 1224 (m), 1145 (s), 1031 (m), 945 (m), 636 (m). FAB LRMS: *m*/*z* 523 ([Cp*(PMe$_3$)Ir(*p*-tolyl)(CO)]$^+$). Anal. Calcd for $C_{22}H_{31}F_3IrO_4PS$: C, 39.34; H, 4.65. Found: C, 39.17; H, 4.47.

[Cp*(PMe$_3$)Ir(2,4,6-trimethylphenyl)(CO)][OTf] (9). Synthesis was performed by employing the general procedure described above using 100 mg (0.176 mmol) of **1** and 36.6 mg (0.247 mmol) of mesitaldehyde. Compound **9** was isolated (89.0 mg, 0.127 mmol) as an ivory-colored powder (72% yield) by precipitation from CH_2Cl_2 solution by addition of Et_2O. Mp: 163 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.87 (s, 1H, $C_6H_2(CH_3)_3$), 6.83 (s, 1H, $C_6H_2(CH_3)_3$), 2.45 (s, 3H, *p*-$C_6H_2(CH_3)_3$), 2.22 (s, 3H, *o*-$C_6H_2(CH_3)_3$), 2.20 (s, 3H, *o*-$C_6H_2(CH_3)_3$), 1.94 (d, $^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.76 (d, $^2J_{P-H}$ = 10.8 Hz, 9H, P(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 169.1 (d, $^2J_{P-C}$ = 17.1 Hz, *C*O), 145.7 (s, *o*-$C_6H_2(CH_3)_3$), 142.8 (d, *J* = 3.0 Hz, *o*-$C_6H_2(CH_3)_3$), 134.9 (s, *p*-$C_6H_2(CH_3)_3$), 129.6 (s, *m*-$C_6H_2(CH_3)_3$), 129.2 (s, *m*-$C_6H_2(CH_3)_3$), 123.8 (s, *i*-$C_6H_2(CH_3)_3$), 104.4 (s, $C_5(CH_3)_5$), 31.1 (s, *o*-$C_6H_2(CH_3)_3$), 30.7 (d, *J* = 5.0 Hz, *o*-$C_6H_2(CH_3)_3$), 20.0 (s, *p*-methyl), 17.1 (d, $^1J_{P-C}$ = 42.3 Hz, P(*C*H$_3$)$_3$), 9.7 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −76.93 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −43.86 (s). IR (CD_2Cl_2): 2015 (s), 1268 (s), 1147 (s), 1031 (s), 638 (s). FAB LRMS: *m*/*z* 551 ([Cp*(PMe$_3$)Ir(2,4,6-trimethylphenyl)(CO)]$^+$). Anal. Calcd for $C_{24}H_{35}F_3IrO_4PS$: C, 41.17; H, 5.04. Found: C, 40.77; H, 5.04.

[Cp*(PMe$_3$)Ir(2-(*Z*)-1-phenylpropenyl)(CO)][OTf] (10). Synthesis was performed by employing the general procedure described above using 103 mg (0.179 mmol) of **1** and 39.2 mg (0.268 mmol) of α-methylcinnamaldehyde. Compound **10** was isolated (91.0 mg, 0.130 mmol) as a beige powder (73% yield) by precipitation from CH_2Cl_2 solution by addition of pentane. Mp: 87 °C dec. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.4−7.1 (m, 5H, C_6H_5), 6.3 (s, 1H, =C*H*Ph), 2.46 (br s, 3H, CCH_3), 2.08 (d,

$^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.86 (d, $^2J_{P-H}$ = 11.2 Hz, 9H, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 167.5 (d, $^2J_{P-C}$ = 12.7 Hz, *C*O), 139.6 (s, *i*-C_6H_5), 136.7 (s, =*C*HPh), 128.6 (s, *o*-C_6H_5), 128.4 (s, *m*-C_6H_5), 126.6 (s, *p*-C_6H_5), 125.4 (d, $^2J_{P-C}$ = 10.6 Hz, *C*CH_3), 121.4 (q, $^1J_{C-F}$ = 319 Hz, *C*F_3), 103.8 (s, $C_5(CH_3)_5$), 34.0 (s, C*C*H_3), 15.5 (d, $^1J_{P-C}$ = 42.6 Hz, $P(CH_3)_3$), 9.4 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −77.00 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −32.59 (s). IR (CD_2Cl_2): 2019 (s), 1384 (m), 1270 (s), 1222 (s), 1149 (s), 1031 (s), 958 (s), 638 (s). FAB HRMS: *m*/*z* calcd for $C_{23}H_{33}IrOP$ 549.1898, found 549.1901. Elemental analysis was not performed for this compound, due to its similarity to complexes **2**−**9**, **14**, and **15**.

[Cp*(PMe$_3$)(Ir(CH$_3$)(η^2(*C*,*C*)-CH$_2$=CHCHO)][OTf] (12). In the glovebox, a 50 mL Schlenk flask was charged with **1** (98 mg, 0.169 mmol) and dichloromethane (6 mL). Acrolein (14.2 mg, 0.254 mmol) was vacuum-transferred from $CaSO_4$ into the reaction vessel. The reaction mixture was stirred at room temperature for 10 days. The volatile materials were removed in vacuo, and the remaining solids were washed with diethyl ether (3 × 10 mL). The crude product was recrystallized twice from dichloromethane/diethyl ether by vapor diffusion at −30 °C to give 66 mg of **12** (63% yield) as a tan powder. Mp: 211 °C. ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.23 (br d, 1H, C*H*O), 3.30 (dddd, $^3J_{H-H}$ = 11.6 Hz, $^3J_{H-H}$ = 7.2 Hz, $^3J_{P-H}$ = 11.1 Hz, $^3J_{H-H}$ = 14.4 Hz, 1H, C*H*CHO), 2.87 (ddd, $^2J_{H-H}$ = 3.2 Hz, $^3J_{H-H}$ = 11.6 Hz, $^3J_{P-H}$ = 8.0 Hz, 1H, *cis*-CH=CH_2), 2.72 (ddd, $^3J_{H-H}$ = 3.2 Hz, $^3J_{H-H}$ = 7.2 Hz, $^3J_{P-H}$ = 10.2 Hz, 1H, *trans*-CH=CH_2), 1.85 (d, $^4J_{P-H}$ = 2.0 Hz, 15 H, $C_5(CH_3)_5$), 1.47 (d, $^2J_{P-H}$ = 8.4 Hz, 9H, $P(CH_3)_3$), 0.81 (d, $^3J_{P-H}$ = 6.4 Hz, 3H, Ir−CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 191.9 (s, *C*HO), 102.9 (d, $^2J_{P-C}$ = 2.3 Hz, $C_5(CH_3)_5$), 59.4 (s, *C*H), 37.8 (s, *C*H_2), 11.5 (d, $^1J_{P-C}$ = 42.5 Hz, $P(CH_3)_3$), 9.4 (s, $C_5(CH_3)_5$), −14.5 (d, $^2J_{P-C}$ = 8.9 Hz, Ir-*C*H_3). ^{19}F NMR (CD_2Cl_2): δ −76.95 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −25.08 (s). IR (CD_2Cl_2): 1677 (s), 1481 (w), 1429 (w), 1384 (m), 1268 (s), 1147 (s), 1031 (s), 960 (s), 636 (s). FAB LRMS: *m*/*z* 475 ([Cp*(PMe$_3$)Ir(CH$_3$)(η^2-(*C*,*C*)-CH$_2$=CHCHO)]$^+$). Anal. Calcd for $C_{18}H_{31}F_3IrO_4PS$: C, 34.66; H, 5.01. Found: C, 34.38; H, 5.02.

[Cp*(PMe$_3$)Ir(CH=CH$_2$)(CO)][OTf] (13). In the glovebox, a 10 mL glass vessel fitted with a Kontes high-vacuum stopcock was charged with acrolein complex **12** (40 mg, 0.064 mmol) and dichloromethane (3 mL). The vessel was sealed and placed in a 75 °C circulating bath for 24 h. After the reaction mixture had cooled to 25 °C, the solvent was removed in vacuo and the remaining solids were washed with diethyl ether (3 × 5 mL). The crude product was recrystallized twice from dichloromethane/diethyl ether by vapor diffusion at −30 °C to give 22 mg of **13** (57% yield) as a tan powder by precipitation from CH_2Cl_2 solution by addition of pentane. Mp: 158−160 °C dec. ^1H NMR (CD_2Cl_2, 400 MHz): δ 6.49 (dd, $^3J_{H-H}$ = 9.2 Hz, $^2J_{H-H}$ = 3.0 Hz, 1H, *trans*-CH=CH_2), 6.40 (ddd, $^3J_{H-H}$ = 16.3 Hz, $^3J_{H-H}$ = 9.2 Hz, $^3J_{H-P}$ = 6.9 Hz, 1H, C*H*=CH$_2$), 5.47 (dd, $^3J_{H-H}$ = 16.6 Hz, $^2J_{H-H}$ = 3.0 Hz, 1H, *cis*-CH=CH_2), 2.02 (d, $^4J_{H-P}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.75 (d, $^2J_{H-P}$ = 9.2 Hz, 9H, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 167.6 (d, $^2J_{C-P}$ = 11 Hz, *C*O), 129.0 (s, CH=*C*H$_2$), 121.5 (q, $^1J_{C-F}$ = 320 Hz, *C*F_3), 118.2 (d, $^2J_{C-P}$ = 12.1 Hz, *C*H=CH$_2$), 103.4 (s, $C_5(CH_3)_5$), 15.2 (d, $^1J_{C-P}$ = 42.7 Hz, $P(CH_3)_3$), 9.4 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −77.0 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −33.8 (s). IR (CD_2Cl_2): 2981 (w), 2973 (w), 2919 (w), 2021 (s), 1575 (w), 1473 (w), 1421 (w), 1384 (m), 1294 (m), 1265 (s), 1224 (m), 1149 (s), 1031 (s), 954 (m), 638 (s), 516 (w). FAB LRMS: *m*/*z* 459 ([Cp*(PMe$_3$)Ir(CH=CH$_2$)(CO)]$^+$). FAB HRMS: *m*/*z* calcd for $C_{16}H_{27}IrOP$ 459.1429, found 459.1423. Elemental analysis was not performed for this compound due to its similarity to complexes **2**−**9**, **14**, and **15**.

[Cp*(PMe$_3$)Ir(*t*-Bu)(CO)][OTf] (14). Synthesis was performed employing the general procedure described above using 135 mg (0.236 mmol) **1**, and 22.4 mg (0.260 mmol) 2,2-dimethylpropanal. Compound **14** was isolated (134 mg, 0.211 mmol) as a white powder (89% yield) by precipitation from CH_2Cl_2 solution by addition of Et_2O. mp = 171−172 °C. ^1H NMR (CD_2Cl_2, 400 MHz): δ 2.02 (d, $^4J_{P-H}$ = 2.4 Hz, 15H, $C_5(CH_3)_5$), 1.84 (d, $^2J_{P-H}$ = 10.4 Hz, 9H, $P(CH_3)_3$), 1.48 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 168.6 (d, $^2J_{P-C}$ = 12.3 Hz, *C*O), 105.7 (d, $^2J_{P-C}$ = 1.7 Hz, $C_5(CH_3)_5$), 41.0 (s, $C(CH_3)_3$), 18.6 (d, $^1J_{P-C}$ = 39.9 Hz, *P*$(CH_3)_3$), 15.5 (d, $^2J_{P-C}$ = 4.8 Hz, *C*$(CH_3)_3$), 10.5 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −77.0 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −47.5 (s). IR (CD_2Cl_2): 2015 (s), 1267 (s), 1222 (m), 1145 (s), 1031 (s), 956 (m), 636 (m). FAB LRMS: *m*/*z* 489 ([Cp*(PMe$_3$)Ir(*t*-Bu)(CO)]$^+$). Anal. Calcd for $C_{19}H_{34}F_3IrO_4PS$: C, 35.73; H, 5.37. Found: C, 35.37; H, 5.16.

[Cp*(PMe$_3$)Ir(*t*-Bu)(CO)][BPh$_4$] (15). Compound **14** (134 mg, 0.211 mmol) was dissolved in 10 mL of CH_2Cl_2. $NaBPh_4$ (404 mg, 1.18 mmol) was added as a solid. The heterogeneous reaction was stirred overnight and then filtered through Celite. The volatile materials were removed in vacuo to give 167 mg (0.207 mmol) of crude **15** in 98% yield. Complex **15** was recrystallized (86% yield) from CH_2Cl_2/toluene and isolated as pale yellow crystals. Mp: 200−201 °C. ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.31 (br s, 8H, *o*-C_6H_5), 7.03 (t, $^3J_{H-H}$ = 6.0, 8H, *m*-C_6H_5), 6.87 (t, $^3J_{H-H}$ = 6.0, 4H, *p*-C_6H_5), 1.96 (d, $^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.69 (d, $^2J_{P-H}$ = 10.6 Hz, 9H, $P(CH_3)_3$), 1.47 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 168.7 (d, $^2J_{P-C}$ = 54.6 Hz, *C*O), 164.5 (1:1:1:1 q, $^1J_{C-B}$ = 48.8 Hz, *i*-C_6H_5), 136.3 (s, C_6H_5), 125.9 (1:1:1:1 q, $^2J_{C-B}$ = 2.8 Hz, *o*-C_6H_5), 122.1 (s, C_6H_5), 105.7 (d, $^2J_{P-C}$ = 2.1 Hz, $C_5(CH_3)_5$), 41.1 (s, $C(CH_3)_3$), 18.7 (d, $^1J_{P-C}$ = 39.8 Hz, $P(CH_3)_3$), 16.3 (d, $^2J_{P-C}$ = 4.6 Hz, *C*$(CH_3)_3$), 10.6 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −45.9 (s). IR (CD_2Cl_2): 3050 (m), 3025 (m), 2996 (m), 2983 (m), 2915 (m), 2850 (m), 2024 (sh), 2005 (vs), 1579 (w), 1479 (m), 1427 (m), 1382 (m), 1363 (w), 1294 (w), 1130 (m), 1029 (w), 954 (s), 732 (s), 707 (s). FAB LRMS: *m*/*z* 489 ([Cp*(PMe$_3$)Ir(*t*-Bu)(CO)]$^+$). Anal. Calcd for $C_{42}H_{53}BIrOP$: C, 62.43; H, 6.49. Found C, 62.33; H, 6.55.

1-Adamantanecarboxaldehyde (16). Although several syntheses of **16** have been reported, a new and more convenient synthesis is described here. A 100 mL three-necked flask, fitted with a nitrogen inlet adapter and two addition funnels, was charged with oxalyl chloride (15 mL, 6.62 mmol) and cooled to −60 °C in a $CHCl_3/CO_2$ bath. One addition funnel was charged with DMSO (0.94 mL, 13.2 mmol) and dichloromethane (5 mL). The other addition funnel was charged with 1-adamantanemethanol (1.00 g, 6.02 mmol), dichloromethane (10 mL), and DMSO (3 mL). The DMSO/CH_2Cl_2 mixture was added to the cold oxalyl chloride dropwise over 3 min. The resulting solution was stirred for 3 min. The DMSO/CH_2Cl_2/1-adamantanemethanol solution was then added dropwise over 2 min, and the addition funnel was rinsed with dichloromethane (2 mL), which was added to the reaction mixture. The resulting reaction mixture was stirred for 15 min. Triethylamine (3.04 g, 3.56 mmol) was added to the clean addition funnel and added dropwise to the reaction mixture over 5 min. The resulting solution was stirred for 5 min. The reaction vessel was removed from the $CHCl_3/CO_2$ bath and warmed to room temperature. Water (40 mL) was added to the mixture and stirred 15 min. The organic materials were extracted into dichloromethane (3 × 30 mL). The combined organic layers were back-extracted with saturated brine solution (40 mL), dried over Na_2SO_4, and filtered, and the solvent was removed in vacuo. The resulting yellow oil was purified by flash column chromatography[160] (silica, 95% hexanes, 5% EtOAc) to afford the aldehyde as a white powder (0.59 g, 3.56 mmol) in 59% yield. ^1H NMR (400 MHz, CD_2Cl_2): δ 9.29 (s, 1H, C*H*O), 2.05 (br m, 3H, β-C*H*), 1.77 (br m, 6H, α-CH_2), 1.70 (br m, 6H, δ-CH_2); lit.[161] δ 9.32 (s, 1H), 2.06 (m, 3H), 1.73 (m, 12H). $^{13}C\{^1H\}$ NMR: δ 206.0 (s, *C*HO), 45.1 (s, α-*C*), 36.9 (s, β-CH_2),

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36.2 (s, γ-CH_2), 27.9 (s, δ-CH); lit.[162] δ 205.88, 41.75, 36.54, 35.83, 27.34. IR (CD_2Cl_2): 2900 (s), 2848 (s), 1726 (s), 1452 (m), 1384 (m), 1349 (m), 1288 (w), 1257 (m), 1193 (m), 1162 (m), 1112 (s), 1089 (s), 1058 (w), 987 (w), 928 (w), 810 (w), 650 (w); lit.[162] ν_{CO} 1730.

[Cp*(PMe$_3$)Ir(1-adamantyl)(CO)][OTf] (17). Synthesis was performed by employing the general procedure described above using 107 mg (0.188 mmol) of **1** and 40.1 mg (0.244 mmol) of 1-adamantanecarboxaldehyde. Compound **17** was isolated (97.1 mg, 0.136 mmol) as a pale yellow powder (72% yield) by precipitation from CH_2Cl_2 solution by addition of pentane. Mp: 125−126 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.19 (br m, 6H), 2.03 (br m, 9H), 1.99 (d, $^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.85 (d, $^2J_{P-H}$ = 10.4 Hz, 9H, P(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 168.1 (d, $^2J_{P-C}$ = 12.2 Hz, *C*O), 105.6 (s, $C_5(CH_3)_5$), 53.1 (d, $^3J_{P-C}$ = 2.2 Hz, β-CH_2), 37.0 (s, δ-CH_2), 33.6 (s, γ-CH), 29.8 (d, $^2J_{P-C}$ = 4.7 Hz, Ir−C), 18.4 (d, $^1J_{P-C}$ = 39.8 Hz, P(CH_3)$_3$), 10.4 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −76.91 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −47.46 (s). IR (CD_2Cl_2): 2915 (m), 2850 (w), 2028 (s), 2021 (s), 1731 (w), 1639 (w), 1450 (m), 1384 (s), 1265 (s), 1149 (s), 1031 (s), 960 (m), 638 (s). FAB LRMS: *m*/*z* 567 ([Cp*(PMe$_3$)Ir(1-adamantyl)(CO)]$^+$). HRMS was not performed for this compound, since the cationic portion is identical with that of complex **18**.

[Cp*(PMe$_3$)Ir(1-adamantyl)(CO)][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (18). Compound **17** (271 mg, 0.379 mmol) was dissolved in 10 mL of CH_2Cl_2. $NaBAr_f$ (1.0 g, 1.1 mmol) was added as a solid. The heterogeneous reaction mixture was stirred overnight and then filtered through Celite. The volatile materials were removed in vacuo to give 536 mg (0.375 mmol) of crude **18** in 99% yield. Complex **18** was recrystallized from CH_2Cl_2/toluene in 81% yield. Mp: 188−191 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.72 (br s, 8H, *o*-$C_6H_3(CF_3)_2$), 7.56 (s, 4H, *p*-$C_6H_3(CF_3)_2$), 2.20 (br m, 6H), 1.97 (d, $^4J_{P-H}$ = 2.0 Hz, 15H, $C_5(CH_3)_5$), 1.88 (br m, 9H), 1.79 (d, $^2J_{P-H}$ = 10.4 Hz, 9H, P(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 168.5 (d, $^2J_{P-C}$ = 12.1 Hz, *C*O), 162.3 (1:1:1:1 q, $^1J_{B-C}$ = 49.5 Hz, *i*-$C_6H_3(CF_3)_2$), 135.3 (br s, *o*-C_6H_3-$(CF_3)_2$), 129.4 (qq, $^2J_{F-C}$ = 31.2 Hz, $^4J_{F-C}$ = 2.9 Hz, *m*-C_6H_3-$(CF_3)_2$), 125.1 (q, $^1J_{F-C}$ = 270.7 Hz, *C*F$_3$), 118.0 (m, *p*-C_6H_3-$(CF_3)_2$), 105.8 (d, $^3J_{P-C}$ = 2.3 Hz, adam-β-CH_2), 37.0 (s, adam-δ-CH_2), 33.9 (s, adam-γ-*C*H), 31.2 (d, $^2J_{P-C}$ = 4.6 Hz, adam-α-*C*), 18.6 (d, $^1J_{P-C}$ = 40.0 Hz, P(CH_3)$_3$), 10.4 (s, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −61.0 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −48.0 (s). IR (CD_2Cl_2): 2931 (m), 2910 (m), 2013 (s), 1612 (m), 1456 (m), 1355 (s), 1278 (s), 1137 (s), 1020 (m), 954 (m), 887 (m), 838 (m), 744 (w), 734 (w), 715 (m), 682 (m), 670 (m). FAB HRMS: *m*/*z* calcd for $C_{24}H_{39}IrOP$ 567.2368, found 567.2382.

[Cp*(PMe$_3$)$_2$Ir(Me)][OTf] (20). Method 1. In the glovebox, a Pyrex NMR tube was charged with **2** (9.4 mg, 0.016 mmol), PMe_3 (6.0 mg, 0.079 mmol), and 0.5 mL of CD_2Cl_2. The tube was then fitted with a Cajon adaptor and flame-sealed in vacuo on a high-vacuum line after two freeze−pump−thaw degas cycles. The tube was photolyzed for 2 h at 10 °C. The ^{1}H and ^{31}P{^{1}H} NMR data matched the data for independently synthesized material exactly.

Method 2. Complex **20** was synthesized independently as follows. In the glovebox, a 20 mL scintillation vial was charged with **1** (29.3 mg, 0.516 mmol) and 2 mL of CH_2Cl_2. To this was added PMe_3 (8.0 μL, 0.775 mmol). When it was mixed, the solution rapidly turned colorless. Removal of the volatile materials in vacuo, followed by precipitation from dichloromethane by addition of pentane, afforded **20** (31.5 mg, 0.490 mmol) in 95% isolated yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 1.79 (t, $^4J_{P-H}$ = 1.9 Hz, 15H, $C_5(CH_3)_5$), 1.54 (m, 18H, P(CH_3)$_3$), 0.16 (t, $^3J_{P-H}$ = 6.3 Hz, 3H, Ir*C*H$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 98.1 (s, $C_5(CH_3)_5$), 17.4 (m, P(CH_3)$_3$), 9.6 (s, C_5-$(CH_3)_5$), −27.8 (t, $^2J_{P-C}$ = 31.6 Hz, IrCH_3). ^{19}F NMR (CD_2Cl_2): δ −77.3 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −42.3 (s). IR (CD_2Cl_2): 2965 (s), 2921 (s), 2829 (m), 2290 (w), 1729 (m), 1640 (w), 1621 (w), 1481 (sh), 1428 (s), 1381 (m), 1274 (s), 1222 (s), 1146 (s), 1070 (w), 1030 (s), 963 (sh), 945 (s), 861 (m), 802 (w), 750 (w), 732 (m), 678 (m), 637 (s), 571 (m), 516 (s). FAB HRMS: *m*/*z* calcd for $C_{17}H_{36}IrP_2$ 495.1921, found 495.1917.

Cp*(PMe$_3$)Ir(*p*-tolyl)(CHO) (28). In the glovebox, a 20 mL scintillation vial was charged with **8** (36.2 mg, 0.054 mmol), 2 mL of THF, and a Teflon-coated stirbar. The mixture was cooled to −30 °C in the glovebox freezer and $LiBEt_3H$ (1 M THF solution, 54 μL, 0.054 mmol) was added by a 100 μL syringe to the stirred solution over 30 s. The vial was returned to the freezer and allowed to stand for 2 h. The mixture was then warmed to 25 °C, and the solvent was removed in vacuo. The remaining solids were extracted with pentane (4 × 2 mL), and the solvent was removed in vacuo from the combined pentane extracts to give **28** (23.5 mg, 0.045 mmol) in 84% isolated yield. The resulting colorless residue was recrystallized in a single crop from dichloromethane in 71% yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 13.8 (d, $^3J_{P-H}$ = 1.7 Hz, 1H, Ir*C*HO), 6.82 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, $C_6H_4CH_3$), 6.71 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, $C_6H_4CH_3$), 2.22 (s, 3H, *p*-CH_3), 1.71 (d, $^4J_{P-H}$ = 1.4 Hz, 15H, $C_5(CH_3)_5$), 1.39 (d, $^2J_{P-H}$ = 10.4 Hz, 9H, P(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 231.6 (br, Ir*C*HO), 141.1 (s, *o*-$C_6H_4CH_3$), 131.0 (s, *p*-$C_6H_4CH_3$), 129.0 (s, *m*-$C_6H_4CH_3$), 128.6 (d, $^2J_{P-C}$ = 12.8 Hz, *i*-$C_6H_4CH_3$), 98.4 (s, $C_5(CH_3)_5$), 20.8 (s, $C_6H_4CH_3$), 15.2 (d, $^1J_{P-C}$ = 39.6 Hz, P(CH_3)$_3$), 9.0 (d, $^3J_{P-C}$ = 12.4 Hz, $C_5(CH_3)_5$). ^{19}F NMR (CD_2Cl_2): δ −77.3 (s). ^{31}P {^{1}H} NMR (CD_2Cl_2): δ −40.0 (s). IR (CD_2Cl_2): 2911 (s), 2864 (s), 2806 (m), 2732 (w), 2569 (w), 2518 (w), 2024 (m), 1978 (w), 1731 (w), 1600 (s), 1563 (m), 1499 (s), 1483 (m), 1455 (m), 1419 (m), 1378 (m), 1281 (m), 1224 (w), 1213 (w), 1156 (w), 1102 (w), 1071 (w), 1054 (w), 1031 (m), 1016 (w), 952 (s), 897 (w), 857 (w), 798 (m), 775 (m), 732 (m), 680 (w), 638 (m), 570 (w), 544 (w), 517 (w), 501 (w). Anal. Calcd for $C_{21}H_{32}IrOP$: C, 48.17; H, 6.16. Found C, 47.80; H, 6.49.

Crystallographic Studies. Crystallographic details are given in Table 4. Crystals of **9**, **15**, and **18** were mounted on quartz fibers using Paratone N hydrocarbon oil. All measurements were made on a Siemens SMART difffractometer with graphite-monochromated Mo Kα radiation. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.30° counted for a total of 10 s each on **9** and **15** and 20 s each on **18**. Data were integrated using the program SAINT[163] and were corrected for Lorentz and polarization effects. No decay corrections were applied. Data were analyzed for agreement and possible absorption using XPREP.[164] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS[164] (**9**, T_{max} = 0.49, T_{min} = 0.28; **15**, T_{max} = 0.69, T_{min} = 0.48; **18**, T_{max} = 0.83, T_{min} = 0.64). The structures were solved by direct methods and expanded using Fourier techniques. Hydrogen atoms were included in calculated idealized positions but not refined. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, (sin θ)/λ, and various classes of indices showed no unusual trends. All calculations were performed using the teXsan[164] crystallographic software package of Molecular Structure Corp.

For complex **9**, the cationic portion was found to be disordered between two sites. Only the Ir(2) and P(2) atoms were located in the minor site of the cation. All non-hydrogen atoms were refined anisotropically, except for Ir(2) and P(2), which were refined isotropically. The population of the majority iridium atom, Ir(1), was allowed to vary, and the populations of Ir(2), P(1), and P(2) were tied to Ir(1); the occupancies of Ir(2) and P(2) were constrained to be (1 − occ(Ir(1))), and the occupancy of P(1) was constrained to equal the occupancy of Ir(1). The isotropic thermal parameters of Ir(2) and P(2) were

(162) Olah, G. A.; Wang, Q. *Synthesis* **1992**, 1090−1092.

(163) SAINT: SAX Area-Detector Integration Program; Version 4.024; Siemens Industrial Automation, Inc., Madison, WI, 1995.

(164) For references providing details of the crystallography techniques, see: Alaimo, P. J.; Bergman, R. G. *Organometallics* **1999**, *18*, 2707−2717.

Table 4. Crystal Data Collection and Refinement Parameters for Complexes 9, 15, and 18

	9	15	18
empirical formula	$C_{24}H_{35}F_3IrO_4PS$	$C_{42}H_{53}BIrOP$	$C_{24}H_{39}IrOP$
fw	699.79	807.88	1522.12
cryst habit	colorless blocks	pale yellow	pale blades
cryst size, mm	0.09 × 0.18 × 0.35	0.15 × 0.16 × 0.30	0.08 × 0.15 × 0.33
cryst syst	triclinic	orthorhombic	monoclinic
lattice type	primitive	primitive	*C*-centered
a, Å	8.5800(4)	20.6674(4)	41.536(2)
b, Å	12.7278(6)	12.2900(2)	12.6740(6)
c, Å	13.0668(6)	29.7698(7)	25.017(1)
α, deg	78.050(1)		
β, deg	70.971(1)		109.960(1)
γ, deg	87.312(1)		
V, Å^3	1319.41(10)	7561.6(2)	12378.7(9)
space group	$P\bar{1}$ (No. 2)	$Pca2_1$ (No. 29)	$C2/c$ (No. 15)
Z value	2	8	8
D_{calcd}, g/cm^3	1.761	1.419	1.633
F_{000}	692.00	3280.00	6064.00
temp, °C	−148.0	−121.0	−130.0
μ(Mo Kα), cm^{-1}	52.62	36.14	23.03
exposure time, s/frame	10.0	10.0	20.0
$2\theta_{max}$, deg	46.6	52.0	53.7
no. of rflns measd			
total	6732	35 069	30 085
unique	3743	14 193	11 622
no. of observns	3518	9152	5376
no. of variables	315	828	754
rfln./param ratio	11.17	11.05	7.13
R;[a] R_w;[b] R_{all}	0.024; 0.033; 0.026	0.027; 0.029; 0.048	0.059; 0.064; 0.128
GOF indicator	1.34	1.01	1.95
max resid density, e/Å^3	0.63	0.85	1.37
min resid density, e/Å^3	−1.67	−0.80	−1.11

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

also constrained to be equal. This model resulted in 5.0% occupancies of Ir(2) and P(2).

For complex **15**, although the anions and the iridium atoms of the cations are related by a noncrystallographic inversion center, addition of the inversion center to the space group operations of $Pca2_1$ does not yield a higher symmetry space group. A view of the asymmetric unit is shown in the supplementary information with only the central atoms labeled. Refinement of the Flack parameter in a test run indicated that the structure reported was the correct enantiomorph. Solution and refinement of the structure was complicated by the pseudo-inversion, by disorder of the iridium center of one cation, and by the presence of a second crystal in the sample (unrecognized at first). Non-hydrogen atoms were refined anisotropically with an occupancy parameter for the disordered iridium atom. Following discovery of the contribution of the second crystal, the six worst reflections with $F_o > F_c$ were removed from the data set. A model including apparent disorder on both iridium atoms drastically reduced the residuals; however, this model could not be refined as well as one including a larger disorder component on only one of the iridium centers. The assignment of disorder to only one of the two molecules is also consistent with the thermal parameters of the other atoms in the two molecules. The final refinement included the occupancy factors of Ir(1) and Ir(3), linked so that they summed to 1.0. The final occupancy ratio Ir(3):Ir(1) was 0.31:0.69. The reduced quality of the data, due to the adhering crystal and the disorder of the structure, indicates that the geometric data should be analyzed with care. The nondisordered molecule clearly shows the expected three-legged piano-stool coordination geometry of the Ir atom by the Cp*, PMe_3, CO, and *tert*-butyl ligands. The majority component of the disordered cation has the same basic geometry, except that the CO ligand is positioned transoid (rather than cisoid) to one of the Cp* methyl groups.

For complex **18**, there are two orientations of the molecule in each site in the ratio 0.216(3):0.784(3). Although the 1-adamantyl and the CO ligands appear to be fully ordered, the Cp* and the PMe_3 ligands are disordered. The majority and minority components of the Ir position are clearly separated, but the positions of the PMe_3 and the Cp* atoms are thoroughly intertwined. Occupancy of all disordered atoms was adjusted to follow the refinement of the Ir(1) and Ir(2) occupancies. The Cp* ligands were refined as rigid groups (using a planar Cp with the methyl groups out of plane by 0.2 Å). Only one atom has been assigned to the minority component of the PMe_3 ligand, P(2), causing the carbon count to be deficient in the refinement. The other fractional carbon atoms on the PMe_3 ligand are apparently masked by the electron density of the major component of the Cp* model.

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Supporting Information Available: Listings of X-ray structural data for complexes **9**, **15**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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